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Intramolecular 1,6-Hydride Transfer in Acyclic 1,6-Diols: A Mechanistic Study

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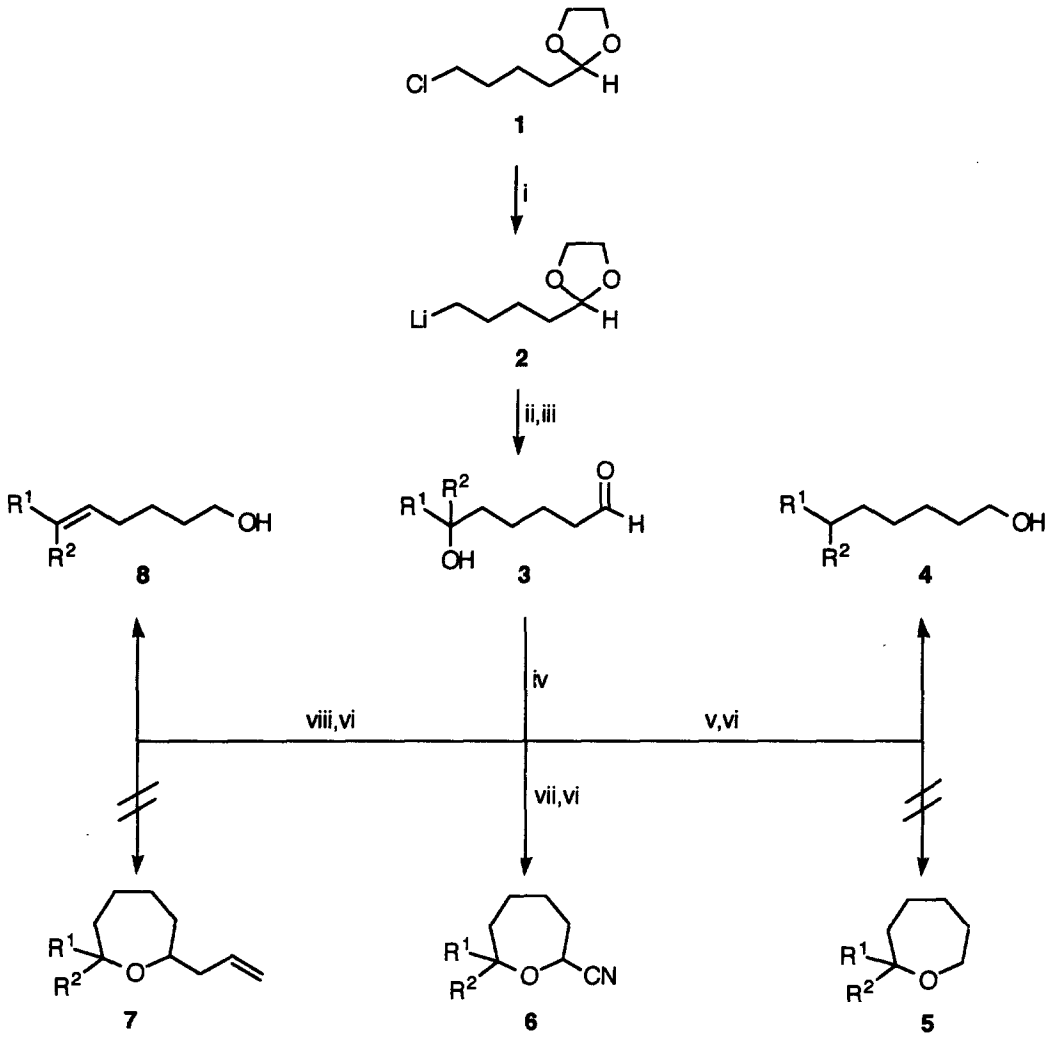
Abstract: The reaction of acyclic 1,6-diol **11a** with 85% phosphoric acid at toluene reflux yields ketone **13a** through an intramolecular 1,6-hydride transfer. This fact is proven by using a deuterated 1,6-diol (**19**), in which the corresponding 1,6-deuteride transfer occurs. A mechanistic proposal through a protonated oxepane (**II**) is formulated, which implies an actual 1,3-hydride transfer; this mechanism differs from the reported one in the literature for cyclic 1,6-diols, in which a real 1,6-hydride transfer takes place due to a proximity effect.

INTRODUCTION

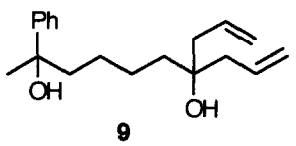
Very recently, and continuing our interest on functionalised organolithium compounds[1], we reported the preparation and synthetic applications of masked δ-lithiocarbonyl compounds[2], starting from the corresponding chlorinated precursor, by a naphthalene-catalysed lithiation[3] at low temperature[4]. Thus, for instance, the pentanal derivative **1** gives, after lithiation (**1**→**2**) and condensation with carbonyl compounds, followed by acid hydrolysis, the corresponding hydroxyaldehydes **3**. When we tried to transform these compounds **3** into the corresponding oxepane derivatives[5] of the type **5-7** using silicon-mediated hydrogenation[6a], allylation[6b] or cyanation[6c,d] the reaction failed in the two first cases yielding the corresponding saturated or unsaturated alcohols **4** and **8**, respectively: only cyanoxepanes **6** could be isolated (Scheme 1)[2]. Considering the described cyclization of ditertiary alcohol **9** with phosphoric acid to the oxepane **10**[7], we thought on the possibility of transforming the hydroxyaldehydes **3** into the corresponding 1,6-diols of the type **9**, by adding an alkyllithium reagent, followed by acid cyclisation to the corresponding oxepane as a route for these heterocycles[5]. We describe here the results obtained: instead of the expected oxepanes the 1,6-diols give, upon acid treatment, ketones resulting from an intramolecular 1,6-hydride transfer.

RESULTS AND DISCUSSION

We first prepared the 1,6-diol **11a** by reaction of the hydroxyaldehyde **3a**[2] [obtained by successive naphthalene-catalysed lithiation of the chloroacetal **1** at low temperature and reaction with cyclohexanone



Scheme 1, *Reagents*: i, Li, naphthalene cat.; ii, R^1R^2CO; iii, HCl-H_2O; iv, $BF_3{\cdot}OEt_2$; v, Et_3SiH; vi, $NaHCO_3$-H_2O; vii, Me_3SiCN; viii, $Me_3SiCH_2CH{=}CH_2$.



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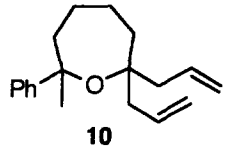

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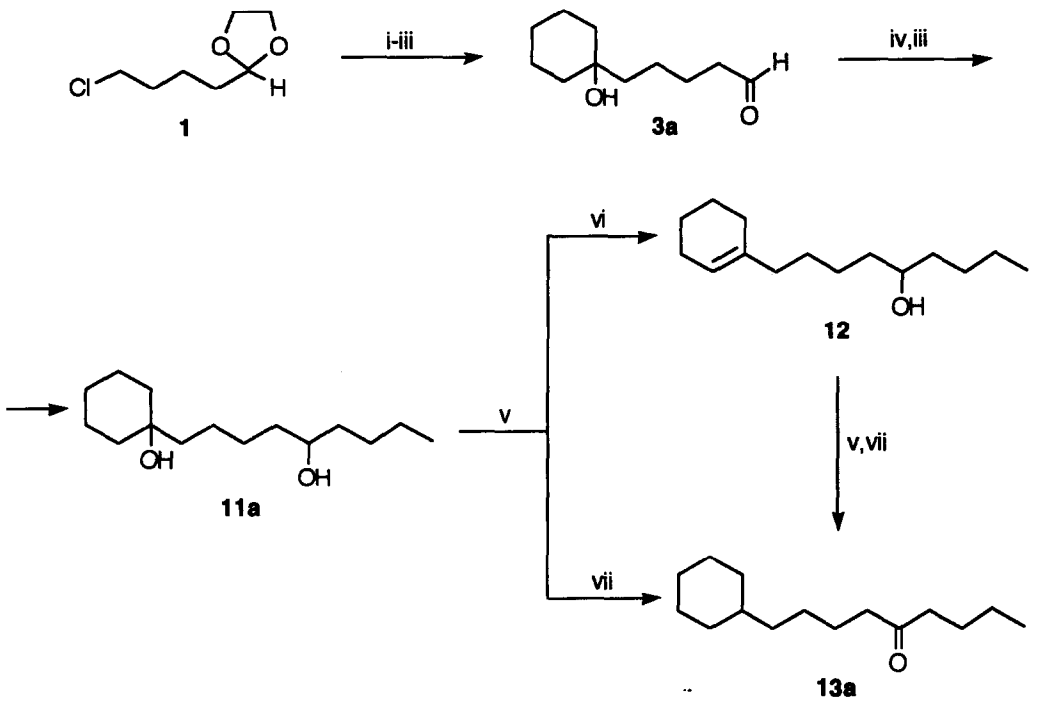
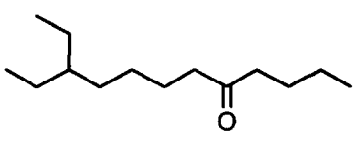
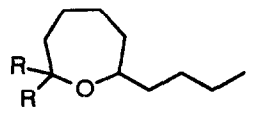
followed by final acid hydrolysis (73% yield)] with *n*-butyllithium (1:2 molar ratio) in THF at temperatures ranging between -78 and 20°C, followed by hydrolysis with aqueous hydrochloric acid, in 39% isolated yield (based on the starting material **1**). The treatment of the diol **11a** with 85% phosphoric acid at room temperature afforded the unsaturated alcohol **12** (75% isolated yield) resulting from a dehydration of the tertiary alcohol giving the corresponding endocyclic olefin. When the same process was carried out at toluene reflux the corresponding ketone **13a** was isolated in 60% yield. A similar yield in compound **13a** (65%) was obtained by refluxing compound **12** in toluene in the presence of 85% phosphoric acid. In no case was the corresponding oxepane **14a** detected (Scheme 2).



Scheme 2. *Reagents and conditions*: i, Li (excess), naphthalene cat. (8 mol %), THF, -78°C; ii, $(\overline{CH_2})_5\overline{CO}$, -78 to 20°C; iii, HCl-$H_2O$; iv, Bu^{n}Li (1:2 molar ratio), -78 to 20°C; v, 85% H_3PO_4, toluene; vi, 20°C; vii, reflux.



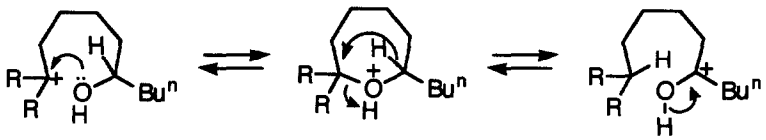
13b



14a : R-R=$(CH_2)_5$
14b : R=Et

The reaction shown in Scheme 2 (**1**→**13a**) is general and can be carried out without isolation of every intermediate. Thus, using 3-pentanone as electrophile (step ii) and following the same protocol as for the ketone **13a**, the expected ketone **13b** was isolated in 30% overall yield (based on the starting chloroacetal **1**). Also in this case the oxepane **14b** was never detected.

Considering the possible mechanism for the transformation of 1,6-diols **11** into ketones **13**, we think that an intramolecular 1,6-hydride transfer takes place. Thus, once the more stable tertiary carbenium ion **I** is formed (either from **11a** or **12**), under the acid reaction conditions, an intramolecular nucleophilic attack of the remaining hydroxy group leads to the protonated oxepane **II**, which suffers a real 1,3-hydride transfer[8] yielding the α-oxygenated carbenium ion **III**, which by final deprotonation yields the ketone **13**[9].



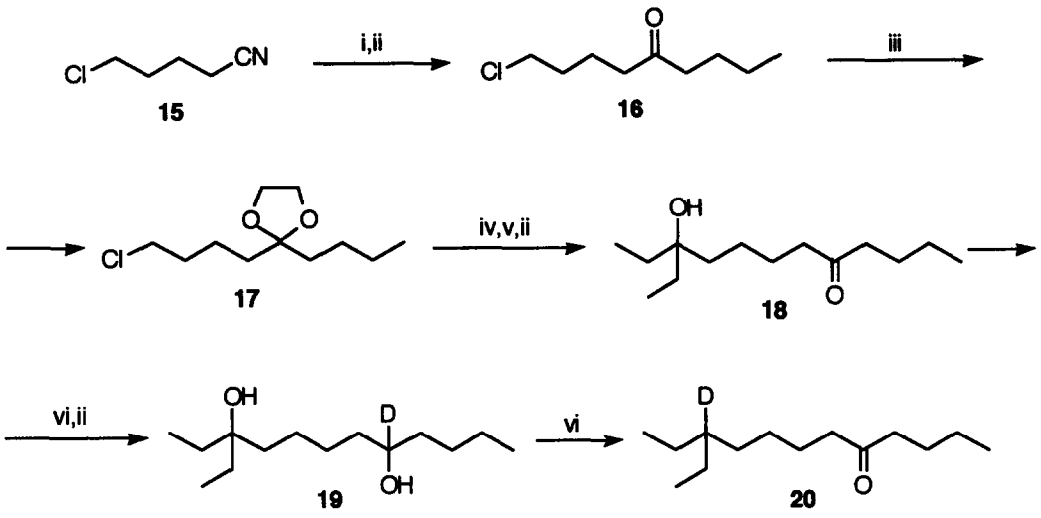
I **II** **III**

In order to prove this apparent 1,6-hydride transfer we prepared the deuterated 1,6-diol **19** as it is shown in Scheme 3. Commercially available 5-chloropentanonitrile (**15**) was reacted with *n*-butylmagnesium bromide giving, after hydrolysis, the corresponding chloroketone **16**[10] (20% isolated yield). After protection of the carbonyl group[11] (**16**→**17**, 85% isolated yield), the lithiation and reaction with 3-pentanone, as above, yielded the hydroxyketone **18** (30% isolated yield, from **17**), which was transformed into the deuterated 1,6-diol **19** by treatment with lithium aluminium deuteride in THF (60% isolated yield). The final reaction of compound **19** with 85% phosphoric acid at toluene reflux afforded the deuterated ketone **20** in 70% isolated yield (>95% deuterium incorporation from mass spectrum) (Scheme 3).

In the literature[12] a transannular 1,6-hydride transfer in 1-methyl-1,6-cyclodecanediol is described: in this case an axial hydride transfer to the tertiary carbocation (**V**) (due to the proximity of both centers) is proposed instead of the 1,3-transfer[8] through the bicyclic protonated ether **VI**, in which an equatorial hydrogen occupies an unfavourable spatial position to be-transfered.

V **VI**

In conclusion, we have proven that the intramolecular 1,6-hydride transfer in acyclic 1,6-diols of the type **11** to give the ketones **13** occurs, probably, through a protonated oxepane of the type **II** and, in fact, it is a 1,3-hydride transfer. This mechanism seems to be different than the proposed one for cyclic 1,6-diols[12], in which the proximity effect of the reactive centers in the cyclic structure permits the 1,6-hydride transfer.



Scheme 3. *Reagents and conditions*: i, Bu^nMgBr, diethyl ether; ii, HCl-H_2O; iii, $HO(CH_2)_2OH$, TsOH cat., benzene; iv, Li excess, naphthalene cat. (8 mol %), THF, -78°C; v, Et_2CO, -78 to 20°C; vi, $LiAlD_4$, THF, 0°C; vi, 85% H_3PO_4, toluene reflux.

EXPERIMENTAL PART

General.-For general information see reference 2. High-resolution mass spectra were performed by the coresponding service at the University of Zaragoza. Compound **3a** was prepared according to the described procedure[2].

Preparation of 1-(1-Hydroxycyclohexyl)-5-nonanol (**11a**).-Once crude compound **3a** was prepared from chloroacetal **1** (2.0 mmol)[2] it was dissolved in THF (5 ml) and the resulting solution cooled to -78°C under an argon atmosphere. To the obtained solution was added a 1.4 M solution of *n*-butyllithium (3.0 ml, 4.2 mmol) and the mixture was stirred 1 h at the same temperature and overnight allowing the temperature to rise to 20°C. Then, the resulting mixture was hydrolysed with water (10 ml), neutralysed with 2 N hydrochloric acid and extracted with diethyl ether (3x10 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel, hexane/ethyl acetate) to give the pure title compound **11a** in 39% overall yield (from starting chloroacetal **1**): R_f 0.55 (hexane/ethyl acetate: 1/1); ν_{max} (film) 3340 (OH), 1130 and 1020 cm^{-1} (C-O); δ_H 0.83 (3 H, t, J=6,9, CH_3), 1.10-1.65 (24 H, m, 12xCH_2), 2.37 (2 H, br s, 2xOH) and 3.45-3.60 (1 H, m, CH); δ_C 13.8, 22.0 (2 C), 22.55 (2 C), 22.7, 25.65, 26.05, 27.65, 36.95, 37.05, 37.15, 37.2, 71.1 and 71.3; *m/z* 224 (M^+-18, 1%), 149 (21), 99 (100), 98 (25), 83 (10), 81 (31), 69 (16), 67 (12), 55 (21), 43 (10) and 41 (13).

Preparation of 1-(Cyclohexenyl)-5-nonanol (**12**).-A mixture of compound **11a** (0.7 mmol) and 85% phosphoric acid (0.1 ml) in toluene (5 ml) was stirred at room temperature for 1 d. The resulting mixture was extracted with diethyl ether (2x5 ml), the organic layer dried over anhydrous sodium sulfate and evaporated (15

Torr). The obtained residue was purified by column chromatography (silica gel, hexane/ethyl acetate) yielding the pure title compound **12** in 75% yield: R_f 0.55 (hexane/ethyl acetate: 4/1); ν_{max} (film) 3340 (OH), 3040, 1650 (HC=C) and 1010 cm^{-1} (C-O); δ_H 0.83 (3 H, t, *J*=7.0, CH_3), 1.10-1.65, 1.70-2.00 (23 H, 2 m, 11xCH_2, OH), 3.49 (1 H, m, CHO) and 5.30 (1 H, m, HC=C); δ_C 13.95, 22.5, 22.7, 22.95, 25.15, 25.3, 27.65, 27.75, 28.15, 37.05, 37.25, 37.9, 71.75, 120.6 and 137.7; *m/z* 224 (M^+, 1%), 149 (32), 136 (11), 135 (52), 123 (12), 122 (100), 121 (33), 113 (26), 108 (29), 107 (34), 96 (10), 95 (32), 94 (43), 93 (51), 91 (12), 85 (10), 83 (10), 82 (19), 81 (73), 80 (21), 79 (74), 77 (14), 69 (29), 68 (14), 67 (67), 57 (17), 55 (29), 54 (10), 53 (13), 43 (14) and 41 (50) (Found: M^+, 224.213692. $C_{15}H_{28}O$ requires 224.214016).

Preparation of 1-Cyclohexyl-5-nonanone (**13a**).-A mixture of compound **11a** (0.5 mmol) and 85% phosphoric acid (0.1 ml) in toluene (5 ml) was refluxed overnight. Then, the resulting mixture was cooled to room temperature and worked up as for compound **12** to give the pure title compound **13a** in 60% yield. The same treatment was carried out starting from compound **12** (65% yield): R_f 0.72 (hexane/ethyl acetate: 9/1); ν_{max} (film) 1710 cm^{-1} (C=O); δ_H 0.90 (3 H, t, *J*=7.3, CH_3), 1.10-1.40, 1.40-1.80 [21 H, 2 m, ring H, $(CH_2)_2CH_2COCH_2(CH_2)_3$] and 2.38 (4 H, t, *J*=7.4, 2xCH_2CO); δ_C 13.8, 22.35, 24.15, 25.95, 26.35 (2 C), 26.45, 26.7, 33.35 (2 C), 37.2, 37.45, 42.5, 42.8 and 211.65; *m/z* 224 (M^+, 3%), 149 (16), 135 (27), 124 (10), 122 (44), 121 (11), 113 (14), 107 (10), 101 (25), 100 (22), 95 (11), 94 (15), 93 (10), 85 (62), 83 (23), 82 (13), 81 (36), 79 (10), 71 (20), 69 (17), 67 (38), 58 (100), 57 (62), 55 (80), 43 (18) and 41 (74) (Found: M^+, 224.213635. $C_{15}H_{28}O$ requires 224.214016).

Preparation of 10-Ethyl-5-dodecanone (**13b**).-This compound was prepared from chloroacetal **1** (2.0 mmol) as it was described for ketone **13a**, without purification of the corresponding intermediates, in 30% overall yield: R_f 0.57 (hexane/diethyl ether: 19/1); ν_{max} (film) 1700 cm^{-1} (C=O); δ_H 0.79 (6 H, t, *J*=7.3, 2xCH_3CH_2CH), 0.86 (3 H, t, *J*=7.4, $CH_3CH_2CH_2$), 1.10-1.35, 1.45-1.65 [15 H, 2 m, $CH_3(CH_2)_2$, $(CH_2)_2CH(CH_2)_3CH_2CO$] and 2.35 (4 H, t, *J*=7.4, 2xCH_2CO); δ_C 10.8 (2 C), 13.8, 22.35, 24.3, 25.35 (2 C), 25.95, 26.4, 32.5, 40.2, 42.5, 42.8 and 211.55; *m/z* 212 (M^+, 4%), 155 (41), 152 (11), 137 (38), 127 (10), 123 (17), 113 (26), 112 (12), 110 (57), 109 (11), 101 (15), 100 (32), 96 (11), 95 (50), 85 (95), 83 (13), 81 (34), 72 (12), 71 (36), 69 (23), 67 (11), 58 (100), 57 (71), 55 (34), 43 (42), 42 (11) and 41 (54) (Found: M^+-H_2O, 194.203019. $C_{14}H_{26}$ requires 194.203451).

Preparation of 1-Chloro-5-nonanone (**16**)[10].-This compound was prepared according to the literature procedure[10] in 20% isolated yield: bp 95-97°C/0.1 Torr (lit. bp 118°C/11 Torr), R_f 0.55 (hexane/ethyl acetate:9/1); ν_{max} (film) 1700 cm^{-1} (C=O); δ_H 0.90 (3 H, t, *J*=7.3, CH_3), 1.20-1.40, 1.50-1.65 [4 H, 2 m, $CH_3(CH_2)_2$], 1.65-2.00 [4 H, m, $(CH_2)_2CH_2Cl$], 2.40, 2.44 [4 H, 2 t, *J*=7.4, 6.8, respectively, $(CH_2)_2CO$] and 3.53 (2 H, t, *J*=6.3, CH_2Cl); δ_C 13.6, 20.85, 22.1, 25.75, 31.75, 41.45, 42.3, 44.5 and 210.45; *m/z* 176 (M+, 4%), 119 (18), 98 (13), 93 (11), 91 (35), 85 (100), 71 (22), 58 (38), 57 (97), 55 (94), 43 (21) and 41 (58).

Preparation of 2-Butyl-2-(4-chlorobutyl)-1,3-dioxolane (**17**).-This compound was prepared from the ketone **17** following the ketalisation general procedure described in the literature[11] in 85% isolated yield: R_f 0.55

(hexane/ethyl acetate: 9/1); ν_{max} (film) 1170 and 1080 cm^{-1} (C-O); δ_H 0.90 (3 H, t, *J*=7.0, CH_3), 1.20-1.40, 1.45-1.65, 1.70-1.90 [12 H, 3 m, 2x$(CH_2)_3CO_2$], 3.53 (2 H, t, *J*=6.7, CH_2Cl) and 3.93 (4 H, s, 2xCH_2O); δ_C 14.0, 21.2, 22.95, 25.95, 32.75, 36.25, 36.85, 44.9, 64.9 (2 C) and 111.5; *m/z* 165 (M^+-55, 34%), 163 (100), 129 (94), 91 (13), 57 (17), 55 (23) and 41 (13).

Preparation of 10-Ethyl-10-hydroxy-5-dodecanone (**18**).-Once the chloroketal **17** (2.0 mmol) was lithiated and reacted with 3-pentanone as it was described for compound **3a** the title compound **18** was obtained in pure form with 30% yield after clolumn chromatography (silica gel, hexane/ethyl acetate): R_f0.57 (hexane/ethyl acetate: 3/2); ν_{max} (film) 3420 (OH), 1700 (C=O) and 1120 cm^{-1} (C-O); δ_H 0.76 (6 H, t, *J*=7.5, 2xCH_3CH_2CO), 0.82 (3 H, t, *J*=7.3, $CH_3CH_2CH_2$), 1.15-1.55 [15 H, m, $CH_3(CH_2)_2$, 2xCH_3CH_2CO, $HOC(CH_2)_3$, OH], 2.31 and 2.33 (4 H, 2 t, *J*=7.4, 7.2, respectively, 2xCH_2C=O); δ_C 7.6 (2 C), 13.7, 22.2, 22.9, 24.3, 25.8, 30.8 (2 C), 37.8, 42.35, 42.55, 74.3 211.3; *m/z* 210 (M^+-18, <1%), 110 (10), 87 (24), 85 (55), 69 (11), 58 (10), 57 (100), 55 (17), 45 (15), 43 (20) and 41 (29).

Preparation of 8-Deuterio-3-ethyl-3,8-dodecanodiol (**19**).-To a suspension of lithium aluminium deuteride (2.0 mmol) in THF (15 ml) was added a solution of the hydroxyketone **18** (0.5 mmol) in THF (5 ml) at 0°C under an argon atmosphere and the resulting mixture was stirred for 5 d allowing the temperature to rise to room temperature. The resulting mixture was then hydrolysed with water (10 ml), neutralised with 2 N hydrochloric acid and extracted with diethyl ether (2x10 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated (15 Torr). The resulting residue was chromatographied (silica gel, hexane/ethyl acetate) to give the pure title compound **19** in 60% yield: R_f0.39 (hexane/ethyl acetate: 4/5); ν_{max} (film) 3360 (OH), 1140 and 1040 cm^{-1} (C-O); δ_H 0.85 (6 H, t, *J*=7.5, 2xCH_3CH_2CO), 0.90 (3 H, t, *J*=6.4, $CH_3CH_2CH_2$) and 1.15-1.60 (20 H, m, 9xCH_2, 2xOH); δ_C 7.7, 7.75, 14.0, 22.7, 23.35, 26.2, 27.75, 30.85, 30.9, 37.0, 37.2, 38.05, 71.15 (t, J_{CD}=21.6, CD) and 74.55; *m/z* 184 (M^+-57, 18%), 138 (12), 97 (18), 96 (13), 95 (10), 88 (25), 87 (90), 86 (11), 85 (17), 70 (31), 69 (25), 58 (17), 57 (100), 56 (12), 55 (24), 45 (32), 43 (42), 42 (18) and 41 (47).

Preparation of 10-Deuterio-10-ethyl-5-dodecanone (**20**).-The deuterated diol **19** (0.25 mmol) was treated with 85% phosphoric acid and the reaction worked up as it was above described for the transformation **11a**→**13a** to give the pure title compound **20** in 70% isolated yield: R_f0.57 (hexane/diethyl ether: 19/1); ν_{max} (film) 1700 cm^{-1} (C=O); δ_H 0.82 (6 H, t, *J*=7.3, 2xCH_3CH_2CD), 0.90 (3 H, t, *J*=7.4, $CH_3CH_2CH_2$), 1.15-1.50, 1.50-1.70 [14 H, 2 m, $(CH_2)_2CD(CH_2)_3$, $CH_3(CH_2)_2$] and 2.39 (4 H, t, *J*=7.4, 2xCH_2CO); δ_C 10.85 (2 C), 13.85, 22.4, 24.35, 25.25 (2 C), 26.0, 26.4, 32.4, 39.65 (t, J_{CD}=18.8, CD), 42.5, 42.85 and 211.7; *m/z* 213 (M^+, 4%), 113 (19), 111 (36), 110 (100), 96 (28), 95 (52), 83 (12), 82 (25), 81 (89), 79 (11), 70 (27), 69 (27), 68 (26), 67 (41), 58 (21), 57 (20), 56 (15), 55 (78), 53 (15), 43 (30), 42 (25) and 41 (94) (Found: M^+, 213.219574. $C_{14}H_{27}DO$ requires 213.220293).

ACKNOWLEDGEMENTS

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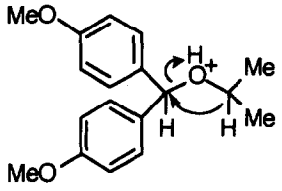

IV

9. One referee suggested that this hydride transfer from the cation **I** seems to be more reasonable than from the protonated oxepane **II**. We thank the referee for this suggestion.
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